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Domino reaction of 3-nitro-2-(trifluoromethyl)-2*H*-chromenes with 2-(1-phenylalkylidene)malononitriles: synthesis of functionalized 6-(trifluoromethyl)-6*H*-dibenzo[*b*,*d*]pyrans and a rare case of [1,5] sigmatropic shift of the nitro group

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ABSTRACT

A variety of functionalized 6-(trifluoromethyl)-6*H*-dibenzo[*b*,*d*]pyrans were easily synthesized in good yields under mild conditions by a domino reaction of 3-nitro-2-(trifluoromethyl)-2*H*-chromenes with 2-(1-phenylethylidene)- and 2-(1-phenylpropylidene)malononitriles. In the latter case, intermediate 7-amino-10-methyl-10-nitro-9-phenyl-6-(trifluoromethyl)-10,10a-dihydro-6*H*-benzo[*c*]chromene-8-carbonitriles were isolated as a result of a rare [1,5] sigmatropic shift of the nitro group.

1. Introduction

Much attention has been addressed to trifluoromethylated heterocyclic compounds because they often show unique biological and physiological activities.[1] In particular, trifluoromethyl-substituted chromones[2] and other six-membered oxygen-containing heterocycles[3] have drawn considerable attention. The search for a simple and efficient access to such compounds with a CF_3 group at a specific position is one of the important goals in this area. However, there are a limited number of regio- and stereoselective syntheses of CF_3-containing 3,4-fused benzopyran derivatives in good yield.

Recently, we reported that the trihalomethylated 3-nitro-2*H*-chromenes could behave as good Michael acceptors in conjugate addition reactions and also act as versatile heterodienes and dipolarophiles in cycloaddition reactions. Thus, the trifluoromethylated pentacyclic lamellarin skeleton have been synthesized by the Grob cyclization from 3-nitro-2-(trifluoromethyl)-2*H*-chromenes **1** and 1-methyl(benzyl)-3,4-dihydroisoquinolines in refluxing isobutanol.[4] 1,3-Dipolar cycloaddition of nonstabilised azomethine ylides to these compounds proceeds diastereoselectively to afford 1-benzopyrano[3,4-*c*]pyrrolidines.[5] Moreover, chromenes **1** undergo heterodiene cycloaddition to 2,3-dihydrofuran and ethyl vinyl ether to give cyclic nitronates with high stereoselectivity and in good yields.[6] The application of this procedure to *N*-cyclohexenylmorpholine led to the corresponding chromeno[3,4-*c*][1,2]benzoxazin-6-oxides.[7] In addition, a two-step formation of 5-(trifluoromethyl)-5*H*-chromeno[3,4-*b*]pyridines in moderate yield was achieved by addition of aminoenones derived from acetylacetone and cyclic amines to 2-CF_3-chromenes **1**, followed by acid hydrolysis and subsequent [1,4]-H shift with intramolecular cyclization.[8]

On the other hand, the dibenzo[*b*,*d*]pyran system constitutes the skeleton of a number of physiologically active natural products and drugs, such as cannabinol, and its derivatives have attracted strong interest due to their useful biological and pharmacological properties.[9] Apart from the various classical approaches towards the synthesis of dibenzo[*b*,*d*]pyrans, a simple and effective procedure for their preparation has been developed recently.[10] Xie et al. obtained the dibenzo[*b*,*d*]pyrans by the domino reaction starting from 2-aryl-3-nitro-2*H*-chromenes and ylidenemalononitriles.[10,11] This promising approach deserves further investigations in order to expand the scope of its possible applications.[12] Herein we wish to demonstrate utility of readily available 3-nitro-2-(trifluoromethyl)-2*H*-chromenes **1** as valuable building blocks for the construction of dibenzo[*b*,*d*]pyrans bearing a CF_3 group at the 6-position via a formal [4+2] cycloaddition of 2-(1-phenylethylidene)malononitrile

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(**2a**) and 2-(1-phenylpropylidene)malononitrile (**2b**). In the latter case, unexpected rearrangement of the initial adducts with participation of the nitro group was observed.

2. Results and discussion

We found that 3-nitro-2-(trifluoromethyl)-2*H*-chromenes **1a**–**d**, which are easily obtainable from the corresponding salicylaldehydes and (*E*)-3,3,3-trifluoro-1-nitroprop-1-ene,[13] reacted with 2-(1-phenylethylidene)malononitrile (**2a**) in the presence of triethylamine in dichloromethane at room temperature to give the desired 7-amino-9-phenyl-6-(trifluoromethyl)-6*H*-benzo[*c*]chromene-8-carbonitriles **3a**–**d** in 33–64% yields. In most cases, the reaction was complete after 6 h and the products could be isolated by simple filtration of the precipitate as white powders. Apparently, the domino Michael addition/cyclization/tautomerization sequence proceeded smoothly, then the elimination of the nitro group took place under these conditions. A plausible pathway leading to the formation of compounds **3** via intermediates **A**, **B**, and **C** is outlined in Scheme 1.[10] Substituents R on the chromene ring had no great effect on the reaction course to give products **3**. However, the electron-donating methoxy group tended to decrease the reactivity. It is necessary to mention that in the case of 3-nitro-2-(trichloromethyl)-2*H*-chromenes, this reaction led to a mixture of starting materials and unidentified products.

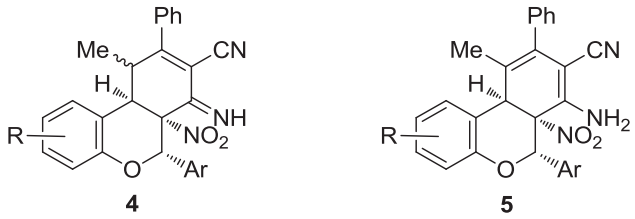
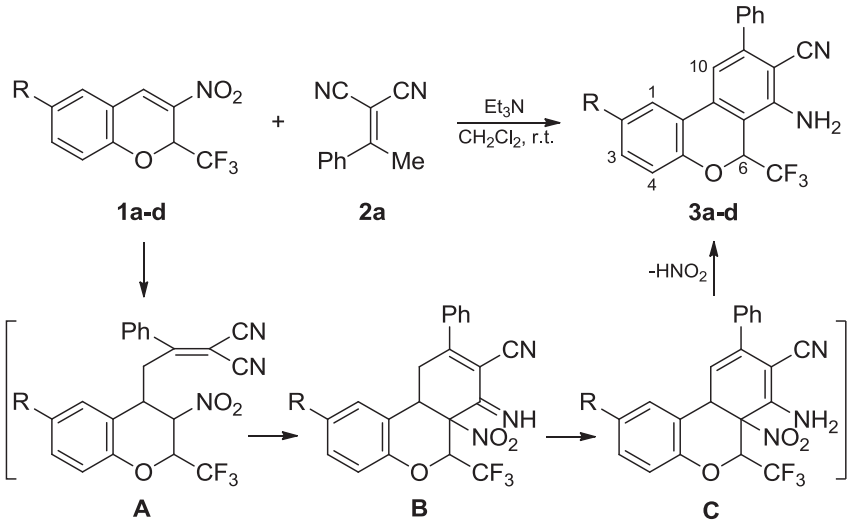


Fig. 1. Structures of products from 2-aryl-3-nitro-2*H*-chromenes and **2b** (Ref. 11).

When 2-CF_3-chromenes **1a**–**d** were allowed to react with malononitrile **2b** under the conditions described above (dichloromethane, rt, 4 h), the reaction unexpectedly provided rearranged intermediates **7a**–**d**, which precipitated from the dichloromethane solution as the sole products in 45–70% yields, instead of affording compounds **6** (Scheme 2). Indeed, close scrutiny of the ^{1}H spectral data provided in Ref. 11 for intermediates **5** revealed that our ^{1}H NMR spectra were similar but inconsistent with the expected structure **6**. This fact led us to believe that the nitro-rearrangement was taking place in the case of chromenes **1**.

The structure of unusual rearrangement products **7** obtained during the preparation of dibenzopyran derivatives **8** was assigned on the basis of NMR and X-ray crystallography data. The characteristic feature of their ^{1}H NMR spectra in DMSO-d_6 is the unusually

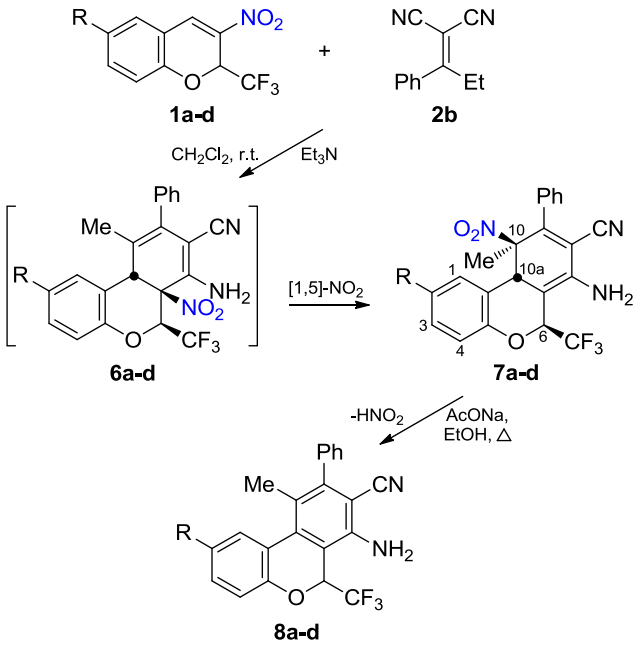


R	**3**	Yield (%)
H	**a**	41
MeO	**b**	33
Br	**c**	64
NO_2	**d**	44

Scheme 1. Synthesis of compounds **3a**–**d**.

Next, we decided to include 2-(1-phenylpropylidene)malononitrile (**2b**) in this study to obtain the corresponding 10-substituted dibenzo[*b*,*d*]pyrans. Previously, it was shown that in contrast to its homologue **2a**, ylidenemalononitrile **2b**, having the ethyl group, reacts with 2-aryl-3-nitro-2*H*-chromenes to give a mixture of two intermediate tautomeric products **4** and **5** (Fig. 1); the stereochemistry of **5** was confirmed by the crystallographic analysis.[11] This indicated that in the case of **2b** spontaneous aromatization does not proceed.

upfield signals from the H-1 aromatic proton (δ 6.07–6.64 ppm for **7a**–**c**) and the Me group (δ 1.50–1.52 ppm); the amino group and the methine H-10a proton appeared as two singlets at δ 5.54–5.78 (2H) and 4.96–5.19 (1H) ppm, while the H-6 proton appeared as a quartet at δ 5.90–6.18 ppm with $^3J_{H,F}$=7.4–7.8 Hz. In the ^{19}F NMR spectrum the CF_3 group manifests itself as a doublet at δ 88.6–88.8 ppm ($^3J_{F,H}$=7.3–7.5 Hz, $CDCl_3$) and δ 90.1–90.7 ppm ($^3J_{F,H}$=7.4–7.8 Hz, DMSO-d_6). Notably, these compounds contain three stereogenic centres, but only one diastereomer could be



R	7	Yield (%)	8	Yield (%)
H	**a**	58	**a**	84
MeO	**b**	45	**b**	89
Br	**c**	70	**c**	72
NO_2	**d**	51	**d**	78

Scheme 2. Synthesis of compounds **7a**–**d** and **8a**–**d**.

observed by ^{19}F NMR spectroscopy of the crude products. In the IR spectra of **7**, highly characteristic amino bands at 3477–3241 cm^{-1}, nitrile absorption at 2217–2231 cm^{-1}, and an intensive absorption band in the range 1538–1548 cm^{-1} for the NO_2 group, were observed.

These data were in good agreement with the structure of compounds **7**, being constructed via a [1,5] sigmatropic nitro-shift. In addition, the regio- and stereochemistry of **7a** and **7b** were unambiguously confirmed by single crystal X-ray diffraction analysis (Figs. 2 and 3). The preferred conformer of **7** is that, which has axial trifluoromethyl and equatorial nitro groups rather than vice versa. It is thus evident from the relative configurations of compounds **5**[11]

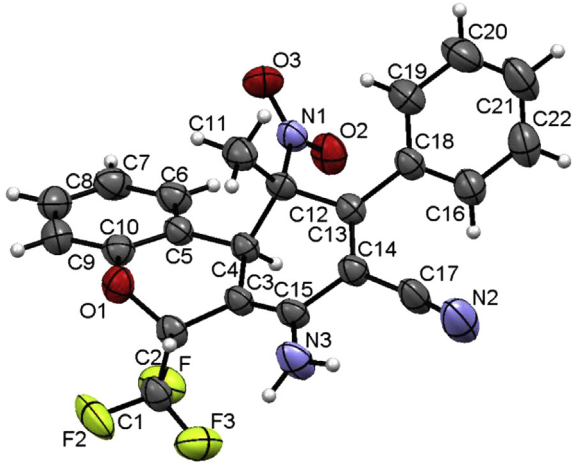


Fig. 2. X-ray crystal structure of **7a** (ORTEP drawing, 50% probability level).

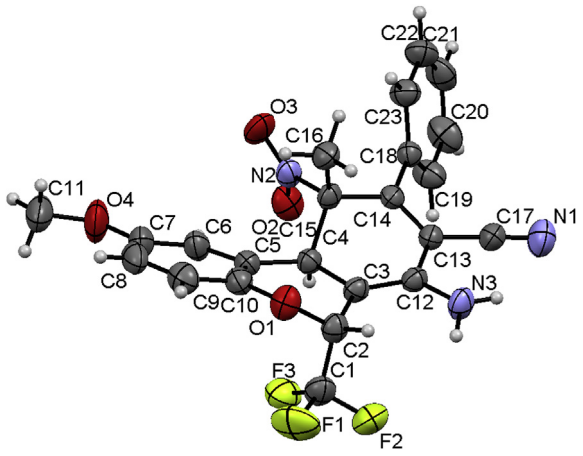


Fig. 3. X-ray crystal structure of **7b** (ORTEP drawing, 50% probability level).

and **7** that the rearrangement cannot involve cationic or radical intermediates, rather a stereospecific sigmatropic pathway is involved. This process is suprafacial as would be required if the new C–NO_2 bond is formed synchronously with the fission of the original C–NO_2 bond.

Obviously, the change in the reaction course is a result of the replacement of the aryl moiety by trifluoromethyl group in the pyran ring. It is likely that this nitro-shift reflects a greater electronic repulsion between the neighbouring CF_3 and NO_2 groups in **6** than that between the Ar and NO_2 in **5**, the consequence being that the trifluoromethyl group and the nitro group are forced to be further apart. Previous reports of [1,5] and [1,3] sigmatropic nitro-shifts are rare and all involve shifts from a tertiary carbon atom to a carbon bearing a hydrogen in a series of adducts from *ipso*-nitration.[14] This type of [1,5] sigmatropic shift, which can be regarded as a migration of the nitro group between two tertiary carbon atoms has not yet been reported in the literature.

While in the solid state compounds **7** were rather stable and could be stored at room temperature, without deterioration, for a long time, in DMSO-d_6 solution they underwent reversible and stereospecific conversion into the corresponding isomers **6**, which had spectroscopic properties very similar to those of the reported compounds **5** (the ^1H NMR signal for the Me group was shifted downfield to δ 2.06–2.12 ppm due to the deshielding effect of the double bond, the methine H-10a proton and the amino group appeared as two singlets at δ 4.26–4.42 and 7.61–7.74 ppm, respectively). Some aromatization by elimination of nitrous acid to form **8** also occurred. The proportions of compounds **6**, **7**, and **8** were determined by integration of the CF_3 signals in the ^{19}F NMR spectra. As can be seen from Table 1, the electron-donating methoxy group facilitates this process, while the electron-withdrawing nitro group makes it slower. Thus, compounds **7** partially isomerized and aromatized when a solution in DMSO-d_6 was allowed to stand at ambient temperature for 6–7 min.

Table 1
Ratio of **6**–**8** after dissolution in DMSO-d_6

7a-d $\rightleftharpoons$ (DMSO-d_6) **6a-d** $\longrightarrow$ **8a-d**

6–8	R	7 (%)	6 (%)	8 (%)
a	H	75	23	2
b	MeO	50	37	13
c	Br	85	14	1
d	NO_2	90	5	5

As would be expected, the nature of the solvent affects the state of this equilibrium. For instance, the equilibrium between isomers **7a**–**c** and **6a**–**c** was almost completely shifted towards rearranged products **7** in $CDCl_3$. The conversion of **7a** into **6a** was followed by monitoring the reaction by ^{19}F NMR spectroscopy at 30 °C. The ratio **7a**:**6a**=88:12 was recorded immediately after dissolving the crystals of **7a** in DMSO-d_6. After 1 h, a 57:42:1 mixture of **7a**, **6a**, and **8a** was present, while after 2 h an equilibrium ratio of 52:47:1 was observed, which remained unchanged for 14 h (51:47:2). The irreversible aromatization stage **7a**⇆**6a**→**8a**, which resulted in a shift of this sigmatropic equilibria toward the dibenzopyran **8a**, was not complete within 7 days and gave a mixture of **7a**:**6a**:**8a**=31:26:43. It should be noted that some decomposition products were also detected in this spectrum after standing in DMSO-d_6 for a week.

Dibenzo[*b*,*d*]pyrans **8a**–**d** were obtained when the domino products **7a**–**d** were heated to reflux in ethanol in the presence of sodium acetate (1 equiv) for 4 h.[10] Thus, the reaction of 2-CF_3-chromenes **1** with ylidenemalononitriles **2** leads to the successful synthesis of dibenzo[*b*,*d*]pyrans **3** and **8** containing a CF_3 group in the pyran ring, a previously unknown group of compounds. The structures of compounds **3** and **8** were confirmed by elemental analysis, ^1H, ^{19}F, ^{13}C NMR, and IR spectroscopy. In the ^{19}F NMR spectra in DMSO-d_6, the trifluoromethyl group appeared as a doublet at δ 86.8–87.5 ppm ($^3J_{F,H}$=7.0 Hz) for **3a**–**d** and 89.0–89.7 ppm ($^3J_{F,H}$=6.7–7.6 Hz) for **8a**–**d**. The ^{13}C NMR spectra of **3a**,**c** showed that the C-6 atom at δ 68.3–69.1 ppm was coupled with the fluorine atoms of the trifluoromethyl group with $^2J_{C,F}$=32.4 Hz; the CF_3 group was observed at δ 124.0–124.4 ppm ($^1J_{C,F}$=288.3 Hz). The absorption bands in the IR spectra of **3** and **8** in the ranges 3490–3241 and 2211–2220 cm^{-1} were attributed to the amino and cyano groups, respectively.

3. Conclusion

In conclusion, we have shown that the domino reaction of 2-(1-phenylalkylidene)malononitriles with 3-nitro-2-(trifluoromethyl)-2*H*-chromenes proceeds smoothly under mild conditions and gives 6-(trifluoromethyl)-6*H*-dibenzo[*b*,*d*]pyrans in moderate to good yields. In the case of 2-(1-phenylpropylidene)malononitrile, a rare case of a [1,5] sigmatropic nitro-shift was found and studied by NMR spectroscopy and X-ray diffraction analysis.

4. Experimental

4.1. General

NMR spectra were recorded on Bruker DRX-400 (^1H—400 MHz, ^{19}F—376 MHz, and ^{13}C—101 MHz) and AVANCE-500 (^1H—500 MHz, ^{19}F—471 MHz, and ^{13}C—126 MHz) spectrometers in DMSO-d_6 and $CDCl_3$ with TMS and C_6F_6 as internal standards, respectively. IR spectra were recorded on a Perkin–Elmer Spectrum BX-II instrument as KBr discs. Elemental analyses were performed at the Microanalysis Services of the Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences. All solvents used were dried and distilled per standard procedures. Melting points were determined on a Differential Scanning Calorimeter NETZSCH DSC 204 F1. The starting 3-nitro-2*H*-chromenes **1a**–**d** were prepared according to the described procedure.[13]

4.2. General procedure for the synthesis of compounds (3a–d)

To a solution of the corresponding 3-nitro-2*H*-chromene **1** (1.0 mmol) and 2-(1-phenylethylidene)malononitrile **2a** (0.17 g, 1.0 mmol) in dry dichloromethane (1 mL) triethylamine (0.10 g, 1.0 mmol) was added over 1 min and the resulting mixture was stirred at room temperature for 6 h. After that, the solid formed was filtered and washed with CH_2Cl_2–hexane (5:1) to give compounds **3** as colourless white powders.

*4.2.1. 7-Amino-9-phenyl-6-(trifluoromethyl)-6H-benzo[c]chromene-8-carbonitrile (**3a**).* Yield 41%, mp 201 °C. IR (KBr) 3472, 3389, 3262, 2211, 1648, 1593, 1557, 1415, 1340 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 6.46 (s, 2H, NH_2), 6.49 (q, *J*=7.0 Hz, 1H, H-6), 7.06–7.14 (m, 2H, H-2, H-4), 7.26 (s, 1H, H-10), 7.38 (t, *J*=7.8 Hz, 1H, H-3), 7.46–7.57 (m, 3H, Ph), 7.58–7.66 (m, 2H, Ph), 8.04 (d, *J*=7.6 Hz, 1H, H-1); ^{19}F NMR (471 MHz, DMSO-d_6) δ 87.2 (d, *J*=7.0 Hz, CF_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 68.3 (q, *J*=32.4 Hz, C-6), 94.0, 105.9, 111.4, 116.6, 117.1, 119.9, 122.9, 124.4 (q, *J*=288.3 Hz, CF_3), 124.9, 128.5, 128.6, 128.7, 131.5, 134.4, 138.4, 147.3, 149.6, 151.8. Anal. Calcd for $C_{21}H_{13}F_3N_2O$: C, 68.85; H, 3.58; N, 7.65. Found: C, 68.90; H, 3.27; N, 7.46.

*4.2.2. 7-Amino-2-methoxy-9-phenyl-6-(trifluoromethyl)-6H-benzo[c]chromene-8-carbonitrile (**3b**).* Yield 33%, mp 298 °C. IR (KBr) 3468, 3384, 3260, 2212, 1646, 1591, 1557, 1489, 1448, 1407, 1343 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 3.79 (s, 3H, MeO), 6.43 (q, *J*=7.0 Hz, 1H, H-6), 6.44 (s, 2H, NH_2), 6.95 (dd, *J*=8.9, 2.9 Hz, 1H, H-3), 7.04 (d, *J*=8.9 Hz, 1H, H-4), 7.33 (s, 1H, H-10), 7.47–7.57 (m, 4H, H-1, Ph), 7.61–7.66 (m, 2H, Ph); ^{19}F NMR (471 MHz, DMSO-d_6) δ 87.5 (d, *J*=7.0 Hz, CF_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.8, 69.9 (q, *J*=32.8 Hz, C-6), 97.5, 108.8, 108.9, 114.4, 116.9, 117.3, 118.0, 120.8, 124.2 (q, *J*=288.3 Hz, CF_3), 128.5, 128.8, 129.1, 135.2, 138.3, 146.1, 147.5, 147.6, 155.4. Anal. Calcd for $C_{22}H_{15}F_3N_2O_2$: C, 66.67; H, 3.81; N, 7.07. Found: C, 66.88; H, 3.63; N, 6.94.

*4.2.3. 7-Amino-2-bromo-9-phenyl-6-(trifluoromethyl)-6H-benzo[c]chromene-8-carbonitrile (**3c**).* Yield 64%, mp 325 °C. IR (KBr) 3473, 3389, 3261, 2215, 1646, 1593, 1555, 1479, 1449, 1425, 1399 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 6.50 (s, 2H, NH_2), 6.52 (q, *J*=7.0 Hz, 1H, H-6), 7.09 (d, *J*=8.7 Hz, 1H, H-4), 7.37 (s, 1H, H-10), 7.47–7.56 (m, 4H, H-3, Ph), 7.65 (d, *J*=7.5 Hz, 2H, Ph), 8.32 (d, *J*=2.1 Hz, 1H, H-1); ^{19}F NMR (376 MHz, DMSO-d_6) δ 87.1 (d, *J*=7.0 Hz, CF_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 70.0 (q, *J*=33.1 Hz, C-6), 98.0, 108.3, 114.4, 115.7, 116.7, 119.1, 122.2, 124.0 (q, *J*=288.1 Hz, CF_3), 127.0, 128.5, 128.9, 129.3, 133.8, 134.1, 138.0, 147.5, 148.0, 151.2. Anal. Calcd for $C_{21}H_{12}BrF_3N_2O$: C, 56.65; H, 2.72; N, 6.29. Found: C, 56.34; H, 2.56; N, 6.21.

*4.2.4. 7-Amino-2-nitro-9-phenyl-6-(trifluoromethyl)-6H-benzo[c]chromene-8-carbonitrile (**3d**).* Yield 44%, mp 291 °C. IR (KBr) 3490, 3403, 3241, 2211, 1636, 1595, 1558, 1523, 1484, 1450, 1411, 1344 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 6.61 (s, 2H, NH_2), 6.68 (br q, *J*=6.1 Hz, 1H, H-6), 7.38 (d, *J*=9.0 Hz, 1H, H-4), 7.48 (s, 1H, H-10), 7.50–7.55 (m, 3H, Ph), 7.66 (br s, 2H, Ph), 8.25 (d, *J*=9.0 Hz, 1H, H-3), 8.94 (s 1H, H-1); ^{19}F NMR (471 MHz, DMSO-d_6) δ 86.8 (br d, *J*=6.0 Hz, CF_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 69.1 (q, *J*=32.4 Hz, C-6), 95.2, 105.5, 111.9, 116.8, 117.9, 120.7, 120.9, 124.0 (q, *J*=288.4 Hz, CF_3), 126.7, 128.5, 128.7, 128.9, 132.3, 138.0, 143.1, 147.8, 149.6, 156.6. Anal. Calcd for $C_{21}H_{12}F_3N_3O_3$: C, 61.32; H, 2.94; N, 10.22. Found: C, 60.92; H, 2.68; N, 10.15.

4.3. General procedure for the synthesis of compounds (7a–d)

To a solution of the corresponding 3-nitro-2*H*-chromene **1** (1.0 mmol) and 2-(1-phenylpropylidene)malononitrile **2b** (0.18 g, 1.0 mmol) in dry dichloromethane (1 mL) triethylamine (0.10 g, 1.0 mmol) was added over 1 min and the resulting mixture was stirred at room temperature for 4 h. After that, the solid formed was filtered and washed with CH_2Cl_2–hexane (5:1) to give compounds **7** as yellow powders.

4.3.1. (6S,10R*,10aR*)-7-Amino-10-methyl-10-nitro-9-phenyl-6-(trifluoromethyl)-10,10a-dihydro-6H-benzo[c]chromene-8-carbonitrile (**7a**).* Yield 58%, mp 160 °C (dec). IR (KBr) 3471, 3395, 3247, 2217, 1659, 1633, 1585, 1538, 1491, 1455, 1386, 1352 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 3H, Me), 3.90 (s, 2H, NH_2), 5.17 (s, 1H, H-10a), 5.29 (qd, J=7.5, 1.2 Hz, 1H, H-6), 6.72 (br d, J=7.6 Hz, 1H, H-1), 6.94 (ddd, J=7.8, 7.4, 1.2 Hz, 1H, H-2), 7.04 (dd, J=8.2, 1.2 Hz, 1H, H-4), 7.25 (td, J=7.8, 1.1 Hz, 1H, H-3), 7.31–7.35 (m, 2H, Ph), 7.42–7.49 (m, 3H, Ph); ^{19}F NMR (376 MHz, $CDCl_3$) δ 88.6 (d, J=7.5 Hz, CF_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.2, 41.1, 70.8 (q, $^2J_{C,F}$=33.4 Hz, C-6), 96.1, 98.0, 111.0, 114.3, 117.8, 117.9, 123.5, 124.4 (q, $^1J_{C,F}$=287.2 Hz, CF_3), 127.5, 127.6, 129.1, 129.7, 130.7, 133.3, 134.0, 153.5, 158.1; ^1H NMR (400 MHz, DMSO-d_6) δ 1.50 (s, 3H, Me), 5.00 (s, 1H, H-10a), 5.57 (s, 2H, NH_2), 5.97 (q, J=7.7 Hz, 1H, H-6), 6.56 (d, J=7.6 Hz, 1H, H-1), 6.94 (td, J=7.6, 1.0 Hz, 1H, H-2), 7.06 (dd, J=8.2, 1.0 Hz, 1H, H-4), 7.27 (td, J=7.7, 1.0 Hz, 1H, H-3), 7.37–7.51 (m, 5H, Ph); ^{19}F NMR (376 MHz, DMSO-d_6) δ 90.5 (d, J=7.7 Hz, CF_3). Anal. Calcd for $C_{22}H_{16}F_3N_3O_3$: C, 61.83; H, 3.77; N, 9.83. Found: C, 61.80; H, 3.73; N, 9.56.

4.3.1.1. (6S,6aS*,10aS*)-7-Amino-10-methyl-6a-nitro-9-phenyl-6-(trifluoromethyl)-6a,10a-dihydro-6H-benzo[c]chromene-8-carbonitrile (**6a**).* ^1H NMR (400 MHz, DMSO-d_6) (23%) δ 2.08 (s, 3H, Me), 4.27 (s, 1H, H-10a), 6.56 (m, 1H, H-6), 7.12–7.50 (m, 9H, Ph), 7.61 (s, 2H, NH_2); ^{19}F NMR (376 MHz, DMSO-d_6) (23%) δ 92.0 (br d, J=7.5 Hz, CF_3).

4.3.2. (6S,10R*,10aR*)-7-Amino-2-methoxy-10-methyl-10-nitro-9-phenyl-6-(trifluoromethyl)-10,10a-dihydro-6H-benzo[c]chromene-8-carbonitrile (**7b**).* Yield 45%, mp 162 °C (dec). IR (KBr) 3467, 3388, 3241, 2218, 1659, 1630, 1543, 1497, 1427, 1384, 1348 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.61 (s, 3H, Me), 3.64 (s, 3H, MeO), 3.89 (s, 2H, NH_2), 5.13 (s, 1H, H-10a), 5.24 (q, J=7.4 Hz, 1H, H-6), 6.24 (d, J=2.9 Hz, 1H, H-1), 6.80 (dd, J=9.0, 2.9 Hz, 1H, H-3), 6.96 (d, J=9.0 Hz, 1H, H-4), 7.31–7.35 (m, 2H, Ph), 7.42–7.50 (m, 3H, Ph); ^{19}F NMR (471 MHz, $CDCl_3$) δ 88.8 (d, J=7.4 Hz, CF_3); ^1H NMR (400 MHz, DMSO-d_6) δ 1.52 (s, 3H, Me), 3.58 (s, 3H, MeO), 4.96 (s, 1H, H-10a), 5.54 (s, 2H, NH_2), 5.90 (q, J=7.8 Hz, 1H, H-6), 6.07 (d, J=2.7 Hz, 1H, H-1), 6.87 (dd, J=8.9, 2.7 Hz, 1H, H-3), 7.00 (d, J=8.9 Hz, 1H, H-4), 7.06–7.10 (m, 2H, Ph), 7.32–7.50 (m, 3H, Ph); ^{19}F NMR (376 MHz, DMSO-d_6) δ 90.7 (d, J=7.8 Hz, CF_3). Anal. Calcd for $C_{23}H_{18}F_3N_3O_4$: C, 60.40; H, 3.97; N, 9.19. Found: C, 60.44; H, 3.94; N, 9.06.

4.3.2.1. (6S,6aS*,10aS*)-7-Amino-2-methoxy-10-methyl-10-nitro-9-phenyl-6-(trifluoromethyl)-10,10a-dihydro-6H-benzo[c]chromene-8-carbonitrile (**6b**).* ^1H NMR (400 MHz, DMSO-d_6) (37%) δ 2.07 (s, 3H, Me), 3.76 (s, 3H, MeO), 4.26 (s, 1H, H-10a), 6.49 (q, J=7.6 Hz, 1H, H-6), 6.83 (d, J=2.8 Hz, 1H, H-1), 6.92 (dd, J=8.8, 2.6 Hz, 1H, H-3), 7.00 (d, J=8.9 Hz, 1H, H-4), 7.32–7.50 (m, 5H, Ph), 7.62 (s, 2H, NH_2); ^{19}F NMR (376 MHz, DMSO-d_6) (37%) δ 92.1 (br s, CF_3).

4.3.3. (6S,10R*,10aR*)-7-Amino-2-bromo-10-methyl-10-nitro-9-phenyl-6-(trifluoromethyl)-10,10a-dihydro-6H-benzo[c]chromene-8-carbonitrile (**7c**).* Yield 70%, mp 171 °C (dec). IR (KBr) 3473, 3392, 3244, 2223, 1660, 1631, 1543, 1481, 1443, 1385, 1349 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.60 (s, 3H, Me), 3.93 (s, 2H, NH_2), 5.12 (s, 1H, H-10a), 5.29 (q, J=7.4 Hz, 1H, H-6), 6.83 (d, J=2.2 Hz, 1H, H-1), 6.93 (d, J=8.7 Hz, 1H, H-4), 7.31–7.34 (m, 2H, Ph), 7.36 (dd, J=8.7, 2.2 Hz, 1H, H-3), 7.43–7.50 (m, 3H, Ph); ^{19}F NMR (471 MHz, $CDCl_3$) δ 88.6 (d, J=7.3 Hz, CF_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.2, 40.8, 70.9 (q, $^2J_{C,F}$=33.6 Hz, C-6), 94.8, 97.8, 100.0, 114.1, 115.8, 119.6, 124.2 (q, $^1J_{C,F}$=287.5 Hz, CF_3), 127.5, 129.0, 129.1, 130.3, 130.8, 132.8, 133.1, 134.3, 152.7, 158.0; ^1H NMR (400 MHz, DMSO-d_6) δ 1.52 (s, 3H, Me), 5.01 (s, 1H, H-10a), 5.65 (s, 2H, NH_2), 6.01 (q, J=7.4 Hz, 1H, H-6), 6.64 (s, 1H, H-1), 7.07 (d, J=8.7 Hz, 1H, H-4), 7.39–7.56 (m, 6H, H-3, Ph); ^{19}F NMR (376 MHz, DMSO-d_6) δ 90.5 (d, J=7.5 Hz, CF_3). Anal. Calcd for $C_{22}H_{15}BrF_3N_3O_3$: C, 52.19; H, 2.99; N, 8.30. Found: C, 51.87; H, 2.94; N, 8.21.

4.3.3.1. (6S,6aS*,10aS*)-7-Amino-2-bromo-10-methyl-10-nitro-9-phenyl-6-(trifluoromethyl)-10,10a-dihydro-6H-benzo[c]chromene-8-carbonitrile (**6c**).* ^1H NMR (400 MHz, DMSO-d_6) (14%) δ 2.06 (s, 3H, Me), 4.32 (s, 1H, H-10a), 6.62 (m, 1H, H-6), 7.34–7.50 (m, 9H, Ph), 7.68 (s, 2H, NH_2); ^{19}F NMR (376 MHz, DMSO-d_6) (14%) δ 92.0 (br s, CF_3).

4.3.4. (6S,10R*,10aR*)-7-Amino-10-methyl-2,10-dinitro-9-phenyl-6-(trifluoromethyl)-10,10a-dihydro-6H-benzo[c]chromene-8-carbonitrile (**7d**).* Yield 51%, mp 171 °C (dec). IR (KBr) 3477, 3381, 3243, 2231, 1662, 1625, 1585, 1548, 1528, 1486, 1443, 1427, 1385, 1344 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.52 (s, 3H, Me), 5.19 (s, 1H, H-10a), 5.78 (s, 2H, NH_2), 6.18 (q, J=7.5 Hz, 1H, H-6), 7.36 (d, J=9.0 Hz, 1H, H-4), 7.40–7.55 (m, 6H, H-1, Ph), 8.19 (dd, J=9.0, 2.3 Hz, 1H, H-3); ^{19}F NMR (376 MHz, DMSO-d_6) δ 90.1 (d, J=7.5 Hz, CF_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.3, 40.9, 71.3 (q, $^2J_{C,F}$=34.0 Hz, C-6), 92.9, 97.5, 110.9, 113.9, 118.3, 118.7, 123.9, 124.0 (q, $^1J_{C,F}$=286.9 Hz, CF_3), 125.5, 127.5, 128.6, 129.1, 129.2, 132.7, 134.9, 143.4, 158.4. Anal. Calcd for $C_{22}H_{15}F_3N_4O_5$: C, 55.99; H, 3.20; N, 11.86. Found: C, 55.92; H, 3.09; N, 11.67.

4.3.4.1. (6S,6aS*,10aS*)-7-Amino-10-methyl-2,10-dinitro-9-phenyl-6-(trifluoromethyl)-10,10a-dihydro-6H-benzo[c]chromene-8-carbonitrile (**6d**).* ^1H NMR (400 MHz, DMSO-d_6) (5%) δ 2.12 (s, 3H, Me), 4.42 (s, 1H, H-10a), 6.59 (q, J=7.5 Hz, 1H, H-6), 7.40–7.55 (m, 5H, Ph), 7.74 (s, 2H, NH_2); ^{19}F NMR (376 MHz, DMSO-d_6) (5%) δ 92.0 (br s, CF_3).

4.4. General procedure for the synthesis of compounds (8a–d)

A solution of the corresponding carbonitrile **7** (1.0 mmol) and sodium acetate (0.08 g, 1.0 mmol) in ethanol (6–8 mL) was refluxed for 4 h. After removal of the solvent under reduced pressure, the residue was washed with water, dried, and recrystallized from CH_2Cl_2–hexane (1:1) to give compounds **8** as colourless powders.

*4.4.1. 7-Amino-10-methyl-9-phenyl-6-(trifluoromethyl)-6H-benzo[c]chromene-8-carbonitrile (**8a**).* Yield 84%, mp 223 °C. IR (KBr) 3482, 3355, 3253, 2220, 1645, 1588, 1570, 1556, 1427 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H, Me), 4.44 (s, 2H, NH_2), 5.62 (q, J=7.2 Hz, 1H, H-6), 7.13 (td, J=7.8, 1.2 Hz, 1H, H-2), 7.16 (dd, J=8.2, 1.2 Hz, 1H, H-4), 7.29–7.37 (m, 3H, H-3, Ph), 7.44–7.54 (m, 3H, Ph), 7.74 (dd, J=8.0, 1.2 Hz, 1H, H-1); ^{19}F NMR (376 MHz, $CDCl_3$) δ 88.0 (d, J=7.2 Hz, CF_3); ^{19}F NMR (376 MHz, DMSO-d_6) δ 89.4 (d, J=7.6 Hz, CF_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.7, 70.6 (q, $^2J_{C,F}$=32.4 Hz, C-6), 100.4, 114.0, 116.6, 117.6, 122.4, 122.7, 124.1, 124.3 (q, $^1J_{C,F}$=288.7 Hz, CF_3), 128.6, 128.7, 128.8, 128.9, 129.0, 129.1, 130.6, 135.8, 138.7, 144.0, 149.0, 153.7. Anal. Calcd for $C_{22}H_{15}F_3N_2O$: C, 69.47; H, 3.97; N, 7.36. Found: C, 69.27; H, 3.92; N, 7.35.

*4.4.2. 7-Amino-2-methoxy-10-methyl-9-phenyl-6-(trifluoromethyl)-6H-benzo[c]chromene-8-carbonitrile (**8b**).* Yield 89%, mp 231 °C. IR (KBr) 3472, 3391, 3358, 3258, 2216, 1646, 1560, 1490, 1424 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.28 (s, 3H, Me), 3.81 (s, 3H, MeO), 4.44 (s, 2H, NH_2), 5.57 (q, J=7.2 Hz, 1H, H-6), 6.90 (dd, J=8.8, 2.9 Hz, 1H, H-3), 7.10 (d, J=8.8 Hz, 1H, H-4), 7.28 (d, J=2.9 Hz, 1H, H-1), 7.29–7.37 (m, 2H, Ph), 7.44–7.54 (m, 3H, Ph); ^{19}F NMR (471 MHz, $CDCl_3$) δ 88.3 (d, J=7.2 Hz, CF_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.6, 55.8, 70.7 (q, $^2J_{C,F}$=32.2 Hz, C-6), 100.5, 114.3, 114.6, 115.7, 116.6, 118.0, 123.3, 124.1, 124.4 (q, $^1J_{C,F}$=289.0 Hz, CF_3), 128.6, 128.7, 128.8, 128.9, 129.1, 135.9, 138.7, 144.0, 147.5, 148.1, 154.5; ^1H NMR (400 MHz, DMSO-d_6) δ 2.15

(s, 3H, Me), 3.75 (s, 3H, MeO), 6.10 (s, 2H, NH_2), 6.30 (q, J=7.2 Hz, 1H, H-6), 6.97 (dd, J=8.8, 2.9 Hz, 1H, H-3), 7.10 (d, J=8.8 Hz, 1H, H-4), 7.30–7.36 (m, 1H, Ph), 7.35 (d, J=2.9 Hz, 1H, H-1), 7.42–7.56 (m, 4H, Ph); ^{19}F NMR (376 MHz, DMSO-d_6) δ 89.7 (d, J=7.2 Hz, CF_3). Anal. Calcd for $C_{23}H_{17}F_3N_2O_2$: C, 67.31; H, 4.18; N, 6.83. Found: C, 66.91; H, 4.19; N, 6.85.

*4.4.3. 7-Amino-2-bromo-10-methyl-9-phenyl-6-(trifluoromethyl)-6H-benzo[c]chromene-8-carbonitrile (**8c**).* Yield 72%, mp 229 °C. IR (KBr) 3480, 3356, 3254, 2220, 1645, 1570, 1553, 1424, 1393 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H, Me), 4.45 (s, 2H, NH_2), 5.62 (q, J=7.1 Hz, 1H, H-6), 7.06 (d, J=8.6 Hz, 1H, H-4), 7.28–7.36 (m, 2H, Ph), 7.44 (dd, J=8.6, 2.3 Hz, 1H, H-3), 7.46–7.55 (m, 3H, Ph), 7.86 (d, J=2.3 Hz, 1H, H-1); ^{19}F NMR (376 MHz, $CDCl_3$) δ 88.0 (d, J=7.1 Hz, CF_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 20.7, 70.9 (q, $^2J_{C,F}$=32.6 Hz, C-6), 101.1, 113.9, 115.0, 116.6, 119.4, 124.3, 124.4 (q, $^1J_{C,F}$=288.6 Hz, CF_3), 124.7, 128.9, 129.1, 129.2, 131.6, 133.4, 134.6, 138.6, 144.2, 149.4, 152.9; ^{19}F NMR (376 MHz, DMSO-d_6) 89.4 (d, J=7.5 Hz, CF_3). Anal. Calcd for $C_{22}H_{14}BrF_3N_2O$: C, 57.54; H, 3.07; N, 6.10. Found: C, 57.48; H, 3.03; N, 6.07.

*4.4.4. 7-Amino-10-methyl-2-nitro-9-phenyl-6-(trifluoromethyl)-6H-benzo[c]chromene-8-carbonitrile (**8d**).* Yield 78%, mp 242 °C. IR (KBr) 3488, 3371, 3250, 2218, 1642, 1621, 1590, 1570, 1521, 1424, 1339 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H, Me), 4.50 (s, 2H, NH_2), 5.76 (q, J=7.0 Hz, 1H, H-6), 7.29 (d, J=8.9 Hz, 1H, H-4), 7.30–7.38 (m, 2H, Ph), 7.47–7.55 (m, 3H, Ph), 8.25 (dd, J=8.9, 2.6 Hz, 1H, H-3), 8.73 (d, J=2.6 Hz, 1H, H-1); ^{19}F NMR (376 MHz, $CDCl_3$) δ 87.6 (d, J=7.0 Hz, CF_3); ^{19}F NMR (376 MHz, DMSO-d_6) 89.0 (d, J=6.7 Hz, CF_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.6, 70.7 (q, $^2J_{C,F}$=33.1 Hz, C-6), 101.7, 113.1, 116.1, 118.2, 123.0, 123.9 (q, $^1J_{C,F}$=288.1 Hz, CF_3), 124.5, 124.7, 125.9, 128.6, 128.8, 128.9, 129.0, 133.3, 138.0, 142.7, 144.2, 149.7, 158.6. Anal. Calcd for $C_{22}H_{14}F_3N_3O_3$: C, 62.12; H, 3.32; N, 9.88. Found: C, 62.15; H, 3.32; N, 9.68.

5. Crystallographic data for compounds 7a and 7b

The X-ray diffraction analysis for the structures of compounds **7a** and **7b** were performed on an Xcalibur 3 automatic four-circle diffractometer (CCD detector) employing graphite monochromated MoKα radiation (λ=0.71073 Å) at temperature 295(2) K and operating in the ω-scans mode. The structures were solved by direct methods and refined with full-matrix least-squares calculation on F2 using SHELX-97.[15] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located geometrically using a riding model.

5.1. Crystal data for 7a

$C_{22}H_{16}F_3N_3O_3$, M=427.38, yellow prisms, triclinic crystals space group $P\bar{1}$, a=8.8332(9), b=10.1374(8), c=11.8973(13) Å, α=71.309(8), β=83.959(9), γ=74.206(8)°, V=970.88(16) Å^3, absorption coefficient μ=0.118 mm^{-1}, Z=2, d_{calcd}=1.462. The final discrepancy factors R_1=0.0402, wR_2=0.0597, GoF=1.002 for 2376 reflections with $I>2\sigma(I)$; R_1=0.1400, wR_2=0.0642 (all data). Largest different peak and hole: 0.190 and −0.161 e Å^{-3}. Completeness to θ=26.00° (84.3%). Deposition number CCDC 942173.

5.2. Crystal data for 7b

$C_{23}H_{18}F_3N_3O_4$, M=457.40, yellow prisms, triclinic crystals space group $P\bar{1}$, a=8.4889(7), b=9.0033(9), c=14.6128(13) Å, α=95.207(8), β=91.971(7), γ=111.839(9)°, V=1029.59(16) Å^3, absorption coefficient μ=0.120 mm^{-1}, Z=2, d_{calcd}=1.475. The final discrepancy factors R_1=0.0380, wR_2=0.0877, GoF=1.005 for 2496 reflections with $I>2\sigma(I)$; R_1=0.0794, wR_2=0.1023 (all data). Largest different peak and hole: 0.293 and −0.153 e Å^{-3}. Completeness to θ=26.00° (94.0%). Deposition number CCDC 942174.

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